

# STUDIES ON KINETICS OF DIMETHYL CARBONATE SYNTHESIS BY HOMOGENEOUS TRANSESTERIFICATION

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## ABSTRACT

A comprehensive kinetic study on dimethyl carbonate synthesis by transesterification of ethylene carbonate with methanol has been conducted. An alkali base metal (KOH) was used as catalyst in the synthesis of DMC and its catalytic ability was investigated in term of kinetics. The reaction orders, the activation energy and the rate constants were determined for both forward and backward reactions. The reaction is reversible and the equilibrium rate constant was estimated to be  $135.77 \exp(-16542.4/RT)$ .

**Keywords :** dimethyl carbonate synthesis, transesterification reaction, kinetic study on DMC synthesis

## INTISARI

Telah dilakukan studi lengkap mengenai kinetik pembuatan dimetil karbonat (DMC) melalui transesterifikasi etilen karbonat dengan methanol. Sebuah alkali metal basa (KOH) digunakan sebagai katalis dalam pembuatan DMC ini dan kemampuan katalitiknya diselidiki dalam bentuk kinetiknya. Ordo reaksi, energi aktivasi dan konstanta laju reaksi ditentukan baik untuk reaksi maju maupun reaksi balik. Reaksi ini bersifat reversibel dan konstanta laju reaksi kesetimbangannya diestimasi mempunyai nilai  $135,77 \exp(-16542,4/RT)$ .

**Kata Kunci :** dimethyl carbonate synthesis, transesterification reaction, studi kinetik pembuatan dimetil karbonat (DMC synthesis)

## INTRODUCTION

Dimethyl carbonate (DMC) is a versatile and nontoxic chemical substance, which is an important chemical material in the current

chemical industry and in the motor fuel industry. It has been proposed as a methylating agent for aromatic compounds, to replace methyl halides and dimethyl sulfate, which are both toxic and corrosive, and as an intermediate in the synthesize polycarbonates and isocyanates, thereby avoiding the need to use phosgene. DMC is also a candidate for replacing tertiary butyl ether (MTBE) as an oxygen-containing additive for gasoline because it has high oxygen content, a good blending octane, low toxicity, and quick biodegradation [1].

A number of DMC synthesis processes have been suggested and some processes have already been commercialized. The classic route to DMC involves the use of phosgene. This route is disadvantaged by the safety problem of handling highly toxic phosgene and the environmental problem of disposing of sodium chloride.

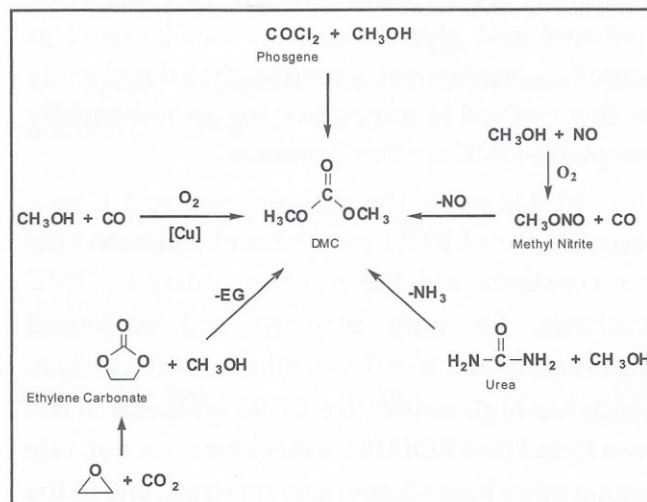


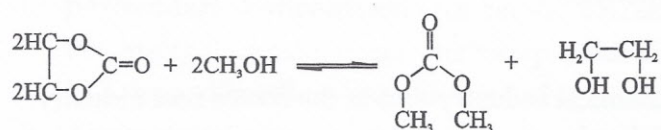
Figure 1. Routes to DMC

Figure 1. shows three routes to DMC: oxidative carbonylation using copper chloride catalyst (actually a redox agent), transesterification between ethylene carbonate and methanol,



and urea methanolysis. Indeed, the transesterification method has been given increasing interest [2, 3].

Overall transesterification reaction of ethylene carbonate (EC) with methanol (MeOH) can be written as follows:



Scheme 1

There are two kinds of transesterification for DMC synthesis: heterogeneous and homogeneous. Tatsumi et.al. [4] introduced heterogeneous catalyst and suggested that a solid base catalyst was excellent for the synthesis of DMC. Watanabe et.al. [5] reported that hydrotalcite-type catalysts have good catalytic ability for DMC synthesis. Knifton et.al. [6] suggested eight classes of catalysts for DMC synthesis through the transesterification reaction.

The homogeneous transesterification method is, however, featured by a large reaction rate and is most likely to be commercialized, though it brings some difficulty in the catalyst separation. A cheap alkali, which is soluble in the methanol and glycol solutions, can be used as homogeneous catalyst. Accordingly, a detail study on this method is imperative for an industrially acceptable DMC synthesis process.

In this work, the authors proposed kinetic performance of KOH catalyst and estimated the rate constants and the reaction orders in DMC synthesis, for both forward and backward reactions. KOH is a base alkali-metal catalyst, which has high activity for DMC synthesis. It has been found that KOH has a moderate reaction rate among other base alkali-metal catalysts, and in the presence of KOH as catalyst, EC conversion in the DMC synthesis could be obtained around 42 % and 55 % in reaction time of 1 and 2 hours, respectively [7]. Moreover, KOH is the cheapest base alkali-metal catalyst.

## EXPERIMENTAL PROCEDURE

All experiments were performed in a stainless-steel autoclave (200 mL) in atmospheric pressure. For mixing in the reaction, magnetic stirrer was used. Reaction temperature was maintained constantly using a temperature controller. A gas chromatograph (Gow-Mac 550P) equipped with a TCD detector and a Carbowax column (1/8 in. 2m, Chrom W-HP, 80/100) was used to analyze the products of reaction. Starting materials used in this work were methanol (purity 99.5%,) produced by Daejung Chemicals & Metals Co., and ethylene carbonate (98% from Aldrich), dimethyl carbonate (99%, Acros) and ethylene glycol (EG) (99%, Daejung) without further purification.

The molar ratio of the initial reactants for forward reaction (MeOH:EC) was in the range of 8:1 - 15:1, while for backward reaction the molar ratio between DMC and EG was changed from 1:10 to 10:1. Potassium hydroxide, soluble in methanol and EG, was used as catalyst for both reactions. Catalyst concentration was maintained around 0.2 wt%. The reaction temperature was varied from 30°C to 60°C and from 30°C to 80°C for forward and backward reaction, respectively.

## RESULTS AND DISCUSSION

The transesterification reaction as shown in Scheme 1 composed of two reactions, that are forward and backward reaction. The rate of reaction of ethylene carbonate (EC) can be expressed as follows:

$$-r_{EC} = k_{forward} C_{MeOH}^a C_{EC}^b - k_{backward} C_{DMC}^c C_{EG}^d \quad (1)$$

When only forward reaction is regarded, the equation (1) can be rearranged to equation (2) since the high concentration of MeOH was used in the reactant for this reaction.

$$-r_{EC} = k_{forward} C_{MeOH}^a C_{EC}^b = k_{forward}^* C_{EC}^b \quad (2)$$



The reaction rate of EC with various initial concentrations is illustrated in Figure 2 at different reaction temperature. The molar ratio of MeOH to EC was maintained with higher than 8 and amount of catalyst was 0.2 wt%. It has been found in the preliminary work [7], that there is no considerable effect of KOH more than 0.2 wt% to EC conversion, while below this amount the catalyst concentration has considerable effect to EC conversion. So, the catalyst amount used in this work was maintained at 0.2 wt%. From the data of Fig. 2, the reaction order was determined by regression based on equation (3) and presented in Table 1.

$$\log(-r_{EC}) = \log k_{forward}^* + b \log C_{EC} \quad (3)$$

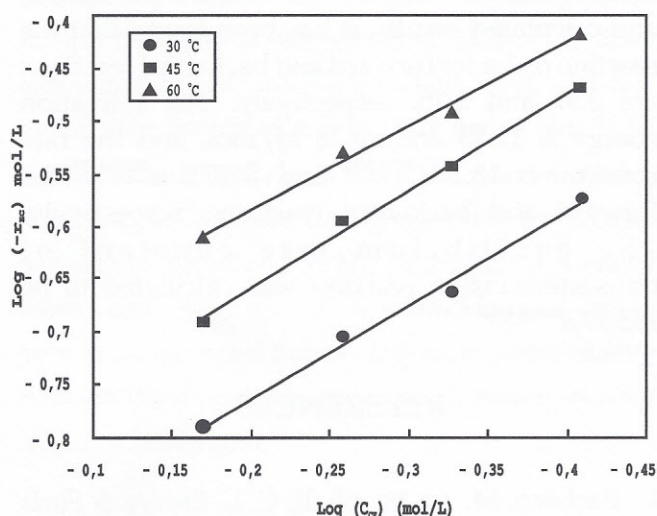


Figure 2. The plot to determine the forward reaction order and constant in DMC synthesis

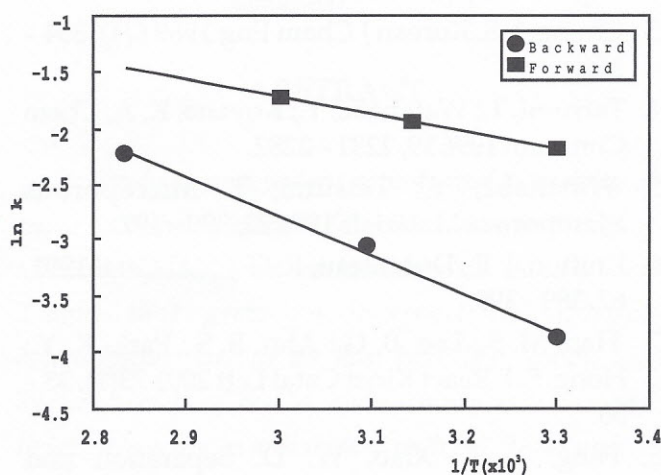


Figure 3. Relationship of k with temperature

The effect of reaction temperature on the reaction rate of EC was investigated by various reaction temperature and the results are plotted in Fig. 2 and 3. As shown in Fig. 2., the reaction rate increased with reaction temperature. The k values were calculated at various temperatures were correlated by eq. (4) and shown in Fig. 3. The activation energy and rate constant were determined and illustrated in Table 1.

$$\ln k = \ln k_o - \frac{E_a}{RT} \quad (4)$$

Table 1. Estimated value of reaction orders and rate constants

Reaction	Reaction order	Activation energy (kJ/mol)	Rate constant
Forward	b = 0.87	12.73	$18.1 e^{-12734.2/RT}$
Backward	c = 1.25, d = 0.9	29.28	$2457.5 e^{-29276.6/RT}$

ing backward reaction, the equation (1) can be rearranged to equation (5).

$$r_{EC} = k_{backward} C_{DMC}^c C_{EG}^d \quad (5)$$

For equal concentrations of DMC and EG, equation (5) becomes

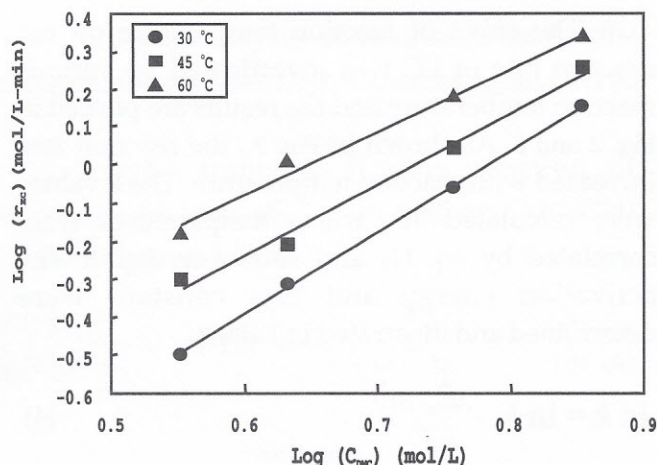
$$r_{EC} = k_{backward} C_{DMC}^c C_{EG}^d = k_{backward} C_{DMC}^{c+d} = k_{backward} C_{DMC}^n \quad (6)$$

and taking logs this gives

$$\log(r_{EC}) = \log k_{backward} + n \log C_{DMC} \quad (7)$$

The overall order of backward reaction was determined by equation (7) as shown in Fig. 4. Knowing the overall order, the reaction order with respect to each component was estimated with the following manipulation.

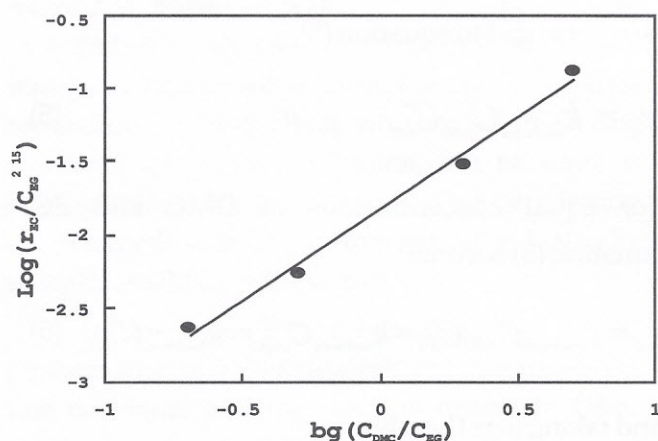




**Figure 4.** The plot to determine the backward overall reaction order and rate constant in DMC synthesis.

$$r_{EC} = k_{backward} C_{DMC}^c C_{EG}^d = k_{backward} C_{DMC}^c C_{EG}^{n-c} = k_{backward} C_{EG}^n \left( \frac{C_{DMC}}{C_{EG}} \right)^c \quad (8)$$

Taking logs and using the value of overall order determined, the reaction order of individual component was calculated with equation (9). In Fig. 5., it was found that the correlation of experiment data to determine the reaction order was well fitted and the values calculated is illustrated in



**Figure 5.** The plot to determine the backward individual reaction order in DMC synthesis.

$$\log \frac{r_{EC}}{C_{EG}^{2.15}} = \log k_{backward} + c \log \frac{C_{DMC}}{C_{EG}} \quad (9)$$

The correlation of  $k$  value with reaction temperature is shown in Fig. 3, the estimated kinetic constants are displayed in Table 1. It is noted that the active energy obtained in this study is comparable with the value presented by Fang et.al. [8]

The reaction equilibrium constant can be calculated as follows:

$$K_{eq} = \frac{k_{backward}}{k_{forward}} \quad (10)$$

Accordingly, with the values of rate constants of forward and backward reactions illustrated in Table 1, the equilibrium rate constant is calculated to be:

$$K_{eq} = 135.77 e^{-16542.4/RT}$$

## CONCLUSIONS

The reaction kinetics and the experimental studies of transesterification reaction of EC with methanol are investigated. From the experimental and calculated results, it has been found that the reaction order for forward and backward reactions are 0.87 and 2.15, respectively. The activation energy is 12.73 and 29.28 kJ/mol, and the rate constant is  $18.1 e^{-12734.2/RT}$  and  $2457.5 e^{-29276.6/RT}$  for forward and backward reactions, respectively. The equilibrium rate constant of transesterification reaction was calculated to be  $135.77 e^{-16542.4/RT}$ .

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